



Mössbauer Study of Relaxation Phenomena in (NH₄)₃FeF₆

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Published in:
Physical Review B

Link to article, DOI:
[10.1103/PhysRevB.8.1020](https://doi.org/10.1103/PhysRevB.8.1020)

Publication date:
1973

Document Version
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):
Mørup, S., & Thrane, N. (1973). Mössbauer Study of Relaxation Phenomena in (NH₄)₃FeF₆. *Physical Review B*, 8(3), 1020-1025. <https://doi.org/10.1103/PhysRevB.8.1020>

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present. The values of the diffusion constants (Table I) are consistent with a donor-donor interaction constant of $C \sim 3 \times 10^{-38} \text{ cm}^6 \text{ sec}^{-1}$. Much of the scatter in the values of the diffusion constant at fixed Pr concentration is attributable to uncertainties in determining the dopant concentrations; however, the reduction in the diffusion constant for the 2-at. % Pr samples as the Nd concentration is raised appears to be systematic. The largest diffusion constants obtained were for the $\text{LaCl}_3\text{:}20\text{-at. \% Pr}$ (0.05- and 0.1-at. % Nd) samples, where $D \sim 5 \times 10^{-9} \text{ cm}^2 \text{ sec}^{-1}$. This diffusion constant is much larger than that obtained by Weber¹ of $6 \times 10^{-10} \text{ cm}^2 \text{ sec}^{-1}$ for 100% $\text{Eu}(\text{PO}_3)_3$ glass. This is not surprising since inhomogeneities in the field seen by the ions at different sites in a glass will shift the donor-ion energy-level positions and this may slow the diffusion considerably.

The diffusion constants for the 20-at. % Pr samples are comparable with that of $2 \times 10^{-9} \text{ cm}^2 \text{ sec}^{-1}$ found by Van der Ziel *et al.* in 10% Er:YF_3 .² Concentration quenching studies of the rare-earth-doped trichlorides have been performed by Gandrud and Moos.¹¹ They find, by a different method, slightly faster diffusion.

If donor-donor transfer is very rapid the exciton can move quickly through the lattice and the exciton diffusion time is no longer the rate-limiting step. In such cases the energy transfer may be limited by the transfer rate between the donor ions and near-neighbor acceptor ions. In the present study the energy transfers investigated have been resonant transfer and exciton migration time was much longer than the near-neighbor transfer rate for all samples studied. Hence, the limit of fast diffusion was not reached.

¹Supported by the U.S. Army Research Office, Durham, N. C.

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Mössbauer Study of Relaxation Phenomena in $(\text{NH}_4)_3\text{FeF}_6$

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(Received 18 July 1972)

The shape of a relaxation-broadened Mössbauer absorption line for a paramagnetic ferric compound is influenced by various terms of the ionic Hamiltonian. Here we discuss especially how the application of an external magnetic field may influence the line shape and may give information about the magnitudes of other terms of the ionic Hamiltonian. Measurements on the two phases of $(\text{NH}_4)_3\text{FeF}_6$ demonstrate differences between cubic and noncubic surroundings of the ferric ion. In the cubic phase we have found a temperature-independent spin-correlation time $\tau \approx 1.19 \times 10^{-10} \text{ sec}$.

I. INTRODUCTION

Mössbauer absorption lines of paramagnetic ferric compounds are often broadened due to electronic relaxation. In some cases a narrowing of the lines has been found when a magnetic field is applied.¹⁻⁶ In the cubic compound ferric alum,⁵ $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, a field of the order of 1 kG reduces the linewidth by about 50%, whereas in the noncubic compound $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ larger fields

are required to produce an effect. Furthermore, in this case the narrowing is less pronounced. In $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$,^{3,4} an asymmetric quadrupole splitting becomes symmetric in a field of about 10 kG. In larger fields the opposite asymmetry is found.⁴ It seems that the influence of the applied field on the spectra depends both on the crystal-field parameters, the magnetic interaction of the ions, and the magnitude of the quadrupole interaction.

In order to further study these phenomena we

have investigated the Mössbauer spectrum of $(\text{NH}_4)_3\text{FeF}_6$ as a function of temperature and applied field. This compound is very suitable for the purpose, as the crystal structure is cubic at room temperature and tetragonal below 263 K.⁷⁻⁹ The ferric ion is situated at face-centered positions surrounded by a fluorine octahedron. The magnetic moment¹⁰ of the ferric ion is close to the spin-only value expected for Fe^{3+} in the $^6\text{S}_{5/2}$ high-spin state.

II. HYPERFINE INTERACTIONS IN PARAMAGNETIC FERRIC COMPOUNDS

In the presence of a nonaxial electric field gradient (EFG) and an applied magnetic field, the interaction between the iron nucleus and its surroundings may be expressed by the Hamiltonian

$$\mathcal{H}_{\text{hf}}(t) = \mathcal{H}_Q + \mathcal{H}_m(t),$$

where

$$\mathcal{H}_Q = \frac{e^2 q Q}{4I(2I-1)} [(3I_z^2 - I^2) + \eta(I_x^2 - I_y^2)]$$

and

$$\begin{aligned} \mathcal{H}_m(t) &= -g\mu_N \vec{I} \cdot \vec{H}_0(t) \\ &= -g\mu_N \vec{I} \cdot [\vec{H}_e(t) + \vec{H}_i(t) + \vec{H}]. \end{aligned}$$

\mathcal{H}_Q is the quadrupole interaction expressed by the conventional symbols and is here assumed to be time independent. The z axis is defined by the principal axis of the EFG. η is the asymmetry parameter describing the deviation from axial symmetry of the EFG.

$\mathcal{H}_m(t)$ describes the magnetic interactions. The electron-nucleus magnetic interaction is here assumed to be isotropic and is described by an effective hyperfine field $\vec{H}_e(t) = A\vec{S}$, where \vec{S} is the ionic spin. The effective-field approximation is valid only if the splitting of the electronic levels is large compared to the hyperfine splitting. In the following we shall assume that this condition is fulfilled. This will normally be the case when the applied field is larger than about 100 G. $\vec{H}_i(t)$ is the fluctuating field due to the surrounding magnetic ions, and \vec{H} is the applied field.

Simplified forms of $\mathcal{H}_{\text{hf}}(t)$ have previously¹¹⁻¹⁶ been used for computation of Mössbauer spectra in the case of fluctuating environments. Here, we shall only discuss cases where the lifetime of the electronic states is of the order of 10^{-9} – 10^{-11} sec, i.e., the paramagnetic hyperfine splitting has collapsed to broadened absorption lines. This situation is often found in paramagnetic ferric compounds.

In the simple case where \mathcal{H}_{hf} is diagonal, i.e., \mathcal{H}_Q is axial and $\vec{H}_0(t)$ fluctuates along the z axis, it is readily shown that the $\pm \frac{3}{2} \leftrightarrow \pm \frac{1}{2}$ nuclear transi-

tions are broader than the $\pm \frac{1}{2} \leftrightarrow \pm \frac{1}{2}$ and $\pm \frac{1}{2} \leftrightarrow \mp \frac{1}{2}$ transitions.^{11,12} This generally results in an asymmetric quadrupole split spectrum. If $\vec{H}_0(t)$ fluctuates perpendicular to the z axis the opposite asymmetry of the spectrum can be found.¹² The difference arises from the off-diagonal elements of $\mathcal{H}_{\text{hf}}(t)$ being capable of inducing transitions between the nuclear sub-states.

For $\mathcal{H}_Q = 0$ and $\vec{H}_0(t)$ fluctuating in random directions, the shape of the Mössbauer spectrum has been calculated¹⁷ by use of Abragam's theory¹⁸ and by use of a perturbation method.¹³ In this case the absorption line does not deviate essentially from a single broad Lorentzian line.

It appears that the direction of the fluctuating magnetic field is decisive for the broadening of the absorption lines. Therefore, we shall discuss this point in greater detail. The dominant term of the magnetic interaction is the electron-nucleus interaction. We therefore consider the spin Hamiltonian of the ferric ion. For simplicity we assume here that the ionic states are separated by energies which are large compared with the hyperfine energies. This is normally the case for $H \gtrsim 100$ G. Thus, neglecting now \mathcal{H}_{hf} , the spin Hamiltonian of the ion may be written¹⁹

$$\mathcal{H}_{\text{ion}} = \mathcal{H}_Z + \mathcal{H}_{\text{dd}} + \mathcal{H}_{\text{ex}} + \mathcal{H}_{\text{cub}} + \mathcal{H}_{\text{ax}} + \mathcal{H}_{\text{rh}}.$$

The terms represent, respectively, the electronic Zeeman interaction, the dipole-dipole interaction and the exchange interaction with the surrounding magnetic ions, and the cubic, axial, and rhombohedral parts of the crystal-field interaction.

It is convenient to describe the dipole-dipole interaction in terms of an internal magnetic field \vec{H}_i , i.e.,

$$\begin{aligned} \mathcal{H}_{\text{dd}} &= \sum_j \{ g^2 \mu_B^2 r_j^{-5} [\vec{S}_j r_j^2 - 3\vec{r}_j (\vec{S}_j \cdot \vec{r}_j)] \} \cdot \vec{S} \\ &= g\mu_B \vec{H}_i \cdot \vec{S}. \end{aligned}$$

\vec{H}_i fluctuates randomly and is normally of the order of 0.1–10 kG, depending on the separation of the magnetic ions. \mathcal{H}_{ex} may often be neglected if the distance between the magnetic ions exceeds several angstroms. \mathcal{H}_{ax} and \mathcal{H}_{rh} may give rise to a splitting of the ionic states of several cm^{-1} , whereas \mathcal{H}_{cub} normally contributes with less than 0.1 cm^{-1} .

On the basis of the expressions for \mathcal{H}_{hf} and \mathcal{H}_{ion} , we are now able to estimate the direction of $\vec{H}_0(t)$ and to discuss the effect of an applied field on the Mössbauer spectrum. Two special cases previously investigated experimentally should be mentioned here.

In ferric alum^{1,5,6,17} the ferric ions are situated in nearly cubic surroundings. Hence $\mathcal{H}_Q \approx 0$ and $\mathcal{H}_{\text{cub}} + \mathcal{H}_{\text{ax}} + \mathcal{H}_{\text{rh}} \lesssim \mathcal{H}_{\text{dd}} + \mathcal{H}_{\text{ex}}$ ($\langle H_i \rangle_{\text{rms}} = 450$ G). For an external field $H \lesssim \langle H_i \rangle_{\text{rms}}$ in the z direction, the ionic states are not eigenstates of S_z , but the ionic

spin direction fluctuates with an average frequency determined by the dipole-dipole and exchange interactions. Consequently the iron nuclei may experience a fluctuating hyperfine field with components both parallel and perpendicular to the z direction. For $\mathcal{K}_{dd} + \mathcal{K}_{ex} \gg \mathcal{K}_z + \mathcal{K}_{cub} + \mathcal{K}_{ax} + \mathcal{K}_{rh}$ the relaxation is isotropic. According to the theory by Bradford and Marshall¹³ an isotropic relaxation can give rise to a spectrum which essentially consists of a single broad Lorentzian line. As the experimental spectra obtained with $H \lesssim 200$ G have Lorentzian shape with a linewidth of about 1.9 mm/sec, they can be interpreted as being caused by isotropic relaxation. Such spectra cannot be produced by longitudinal relaxation alone.

Larger external fields cause a decrease in the linewidth, and for $H > 1.5$ kG the spectra consist of a mixture of broad and narrow components which are independent of the field strength. This is typical for longitudinal relaxation when the spin correlation time is of the order of 1.0 nsec. As now $\mathcal{K}_z \gg \mathcal{K}_{dd} + \mathcal{K}_{ex} + \mathcal{K}_{cub} + \mathcal{K}_{ax} + \mathcal{K}_{rh}$, the ionic states are, to a good approximation, eigenstates of S_z . $\mathcal{K}_{dd} + \mathcal{K}_{ex}$ may now be treated as a perturbation which gives rise to transitions among the eigenstates. Consequently the nuclei may experience a hyperfine field which fluctuates along the z direction.

In $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$,^{3,4} $\mathcal{K}_Q \neq 0$ and $\mathcal{K}_{ax} \gg \mathcal{K}_{dd} + \mathcal{K}_{ex} + \mathcal{K}_{cub} + \mathcal{K}_{rh}$. In the absence of an applied field, $\vec{H}_0(t)$ fluctuates along the z direction defined by the EFG principal axis, i. e., \mathcal{K}_{hr} is diagonal. At large applied fields we obtain $\mathcal{K}_z \gg \mathcal{K}_{ax}$ and the hyperfine field now fluctuates along the direction of the applied field. For polycrystalline samples this direction will be accidental compared to the direction of the principal axis of the EFG, and consequently \mathcal{K}_{hr} will no longer be diagonal. In this case the spectrum may change as a function of H until a saturation is reached when $\mathcal{K}_z \gg \mathcal{K}_{ax}$.

III. EXPERIMENT

Mössbauer spectra of polycrystalline $(\text{NH}_4)_3\text{FeF}_6$ were obtained using a 10-mCi Co^{57} source in the Pd matrix. An ordinary constant-acceleration Mössbauer spectrometer was used with the multiscanning analyzer in the multiscaling mode. The absorber temperature was varied from 78 to 348 K and controlled within 0.1 K. Magnetic fields were applied both parallel and perpendicular to the γ -ray direction. Field strengths from 130 G to 14 kG were used.

A special feature of the spectrometer was an autocycle mode in which the magnetic field was changed during the print-out period between the measurements. A maximum of ten preset values of the magnetic field were possible in a single set-up, thereby providing an efficient data accumulation. The data were handled on a computer, using

a least-squares-fitting procedure.

IV. RESULTS

All the Mössbauer spectra obtained have in common that they consist of a single broad absorption line. However, both the linewidth and the line shape depend on the temperature as well as on the applied magnetic field. In the following we shall discuss the various effects separately.

A. Cubic Phase

Above the transition temperature, the cubic structure implies that $\mathcal{K}_Q = 0$ and $\mathcal{K}_{ax} = \mathcal{K}_{rh} = 0$. For Fe^{+3} surrounded by a fluorine octahedron in the isomorphous compound K_2NaGaF_6 ,²⁰ $\mathcal{K}_{cub} \approx 0.01 \text{ cm}^{-1}$; in other cubic compounds containing the FeF_6^{-3} complex,²¹ \mathcal{K}_{cub} causes a splitting of the same order of magnitude. Therefore it is reasonable to assume that \mathcal{K}_{cub} is small in $(\text{NH}_4)_3\text{FeF}_6$, too. It is also possible to estimate the magnitude of the internal field H_i . For a fcc lattice an explicit formula for $\langle H_i \rangle_{\text{rms}}$ has been found.²²⁻²⁴ Using this we find $\langle H_i \rangle_{\text{rms}} = 1180 \text{ G}$ for $(\text{NH}_4)_3\text{FeF}_6$. The separation of the Fe ions is 6.3 \AA .⁸ Hence \mathcal{K}_{ex} may be neglected. Therefore, for small values of the applied field, \mathcal{K}_{dd} is the dominant term of \mathcal{K}_{ion} . This means that the hyperfine field may fluctuate in random directions. For $H \gg H_i$ the hyperfine field fluctuates along the direction of H , and as $\mathcal{K}_Q = 0$, \mathcal{K}_{hr} becomes diagonal.

The circumstances mentioned above are equivalent to those found in ferric alum. Therefore, a pronounced narrowing of the absorption line should be expected when a field $H \gg \langle H_i \rangle_{\text{rms}}$ is applied. This is actually the case and is demonstrated in Fig. 1(b). The narrowing is completed at $H \approx 3.5 \text{ kG}$, i. e., at $H \approx 3 \langle H_i \rangle_{\text{rms}}$. It is noteworthy that also in ferric alum the saturation takes place for $H \approx 3 \langle H_i \rangle_{\text{rms}}$. This relation may be a characteristic of this class of compounds.

Mössbauer spectra obtained at 273 K and at different applied fields are shown in Fig. 2. The linewidth [full width at half-maximum (FWHM)] of the 130-G spectrum is 0.95 mm/sec. A spectrum broadened to this extent by longitudinal relaxation should contain distinguishable broad and narrow components.⁶ However, as shown in the figure, this spectrum is excellently fitted with a single Lorentzian line. This suggests that the relaxation is isotropic as in the case of ferric alum at small applied fields.

For determination of the linewidth shown in Fig. 1 as a function of the applied field, single Lorentzian fits were used. The high-field spectra deviate little but distinctly from the best fit, being more pointed at the bottom and more flat at the wings. In Figs. 2(b) and 2(c) are shown fits based on the theory of longitudinal relaxation described in Sec.

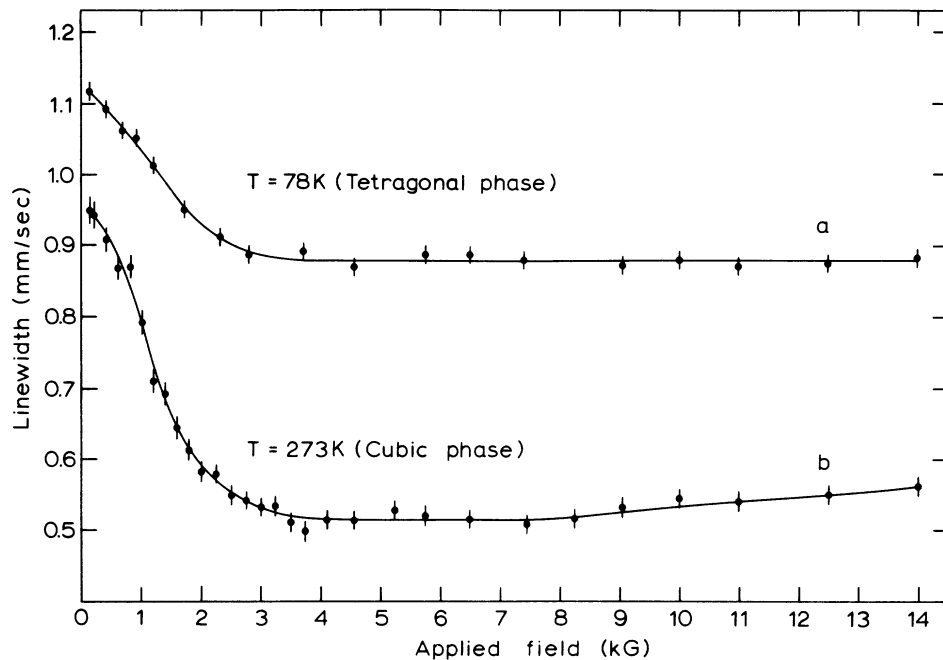


FIG. 1. Mössbauer linewidth (FWHM of the best-fitted Lorentz line) as a function of the applied field. The field was perpendicular to the γ -ray direction. (a) 78 K (tetragonal phase); (b) 273 K (cubic phase).

IV C. These fits are in excellent agreement with the measured spectra.

B. Tetragonal Phase

Below the transition temperature the tetragonal structure implies that $\mathcal{H}_Q \neq 0$, but due to the axial symmetry $\eta = 0$. Also, $\mathcal{H}_{rh} = 0$. $\langle H_i \rangle_{rms}$ may be slightly larger than in the cubic phase, due to lattice contraction. The linewidth as a function of the

applied field at 78 K is shown in Fig. 1(a). It appears that the general behavior is similar to that found at 273 K, namely, a narrowing of the line when the applied field is increased until a saturation takes place. However, the line is somewhat broader and the narrowing is less pronounced than in the cubic phase. This must be due to the quadrupole splitting, which makes the diagonalization of \mathcal{H}_{hf} impossible. It is remarkable that the satu-

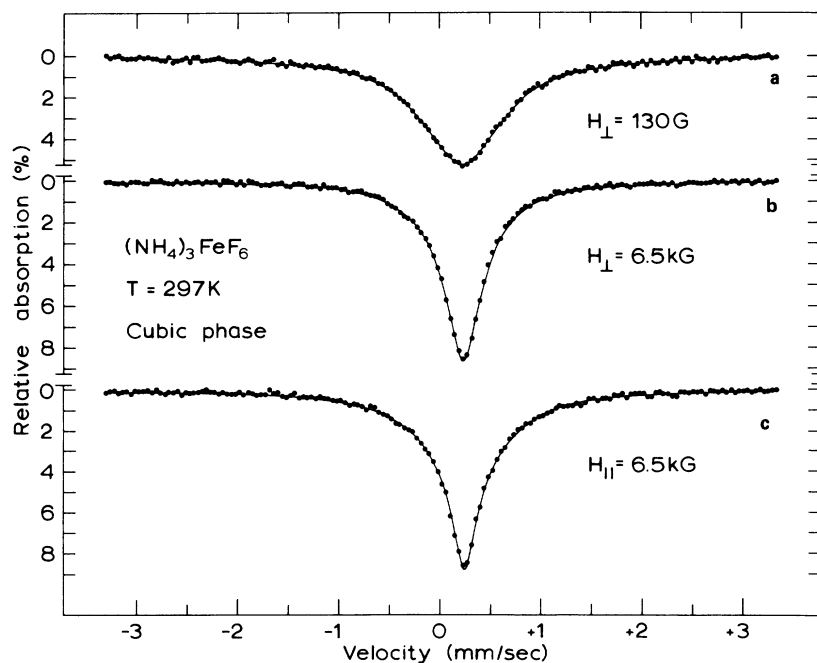


FIG. 2. Mössbauer spectra of $(\text{NH}_4)_3\text{FeF}_6$ obtained to 297 K. (a) $H_{\perp} = 130 \text{ G}$ (the solid line represents the best-fitted Lorentz line, which has the linewidth 0.95 mm/sec). (b) and (c) $H_{\perp} = 6.5 \text{ kG}$ and $H_{\parallel} = 6.5 \text{ kG}$, respectively. Here the solid line represent the best fitting based on theory (see text).

ration is reached at roughly the same field strength as in the cubic phase, as the applied field now must dominate not only the dipole field H_i , but also the crystal field. This leads us to the conclusion that $\mathcal{K}_{dd} > \mathcal{K}_{cub} + \mathcal{K}_{ax}$, i. e., that the crystal-field splitting is less than 0.1 cm^{-1} .

Mössbauer spectra obtained at 78 K with 130-G and 14-kG applied fields are shown in Fig. 3. As expected, for a relaxation-broadened quadrupole split spectrum the 130-G spectrum is asymmetric. However, the 14-kG spectrum is essentially symmetric. This is explained by the fact that \vec{H}_e now fluctuates in the applied-field direction, which is accidental compared to the EFG principal axis. One might expect an opposite asymmetry when a strong field is applied, as seen in the case of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$.⁴ However, the broadening of the lines will depend on the magnitude of \mathcal{K}_Q .¹² For small values of \mathcal{K}_Q the $\pm \frac{3}{2} \rightarrow \pm \frac{1}{2}$ nuclear transitions will remain as the broader components, while for larger values of \mathcal{K}_Q the asymmetry is reversed. Here we believe that we have an intermediate magnitude of \mathcal{K}_Q which results in an equal broadening of nuclear transitions.

C. Spin Correlation Time

In a cubic compound subject to a large applied field the hyperfine Hamiltonian is reduced to

$$\begin{aligned} \mathcal{H}_{hf} &\simeq -\mu_N g [\vec{H}_e(t) + \vec{H}] \cdot \vec{I} \\ &\simeq -\mu_N g [H + \langle H_e \rangle_{av} + h(t)] I_z. \end{aligned}$$

Here the z axis is defined by the applied field, and $H_e(t)$ is divided up into two parts: $H_e(t) = \langle H_e \rangle_{av} + h(t)$.

$\langle H_e \rangle_{av}$ is the average of $H_e(t)$ during a time interval which is long compared with the spin correlation time; $h(t)$ is the remaining fluctuating part of $H_e(t)$. For $H + \langle H_e \rangle_{av} \lesssim 5 \text{ kG}$ we may approximate

$$\mathcal{H}_{hf} \simeq -\mu_N g h(t) I_z.$$

The Mössbauer spectrum corresponding to this simple Hamiltonian will, for spin correlation times $\tau \lesssim 10^{-9} \text{ sec}$, consist of the sum of three Lorentzian lines.^{5,6} The individual linewidths are given by

$$\Gamma = \Gamma_0 + \nu(m_e, m_g)^2 \langle h(t)^2 \rangle_{av} \tau.$$

Γ_0 is the thin-absorber linewidth in the absence of relaxation broadening and $\nu(m_e, m_g)$ is the difference between the z components of the nuclear magnetic moments of the excited state and the ground state of the nucleus.

In Figs. 2(b) and 2(c) are shown computer fits of spectra obtained at 297 K with $H = 6.5 \text{ kG}$ perpendicular to and parallel to the γ -ray direction. The relative intensities of the three Lorentzian lines corresponding to the $\pm \frac{3}{2} \rightarrow \pm \frac{1}{2}$, $\pm \frac{1}{2} \rightarrow \pm \frac{1}{2}$, and $\pm \frac{1}{2} \rightarrow \mp \frac{1}{2}$ nuclear transitions are 3:4:1 and 3:0:1, respectively. In the fitting procedure we maintained $\Gamma_0 = 0.23 \text{ mm/sec}$, which was the experimental linewidth of our Co^{57} source against a thin absorber of metallic iron. For both directions of H the best fit was obtained when $\langle h^2 \rangle_{av} \tau = 19.3 \text{ G}^2 \text{ sec}$. Assuming $\langle h^2 \rangle_{av} = 162 \times 10^9 \text{ G}^2$, which is a typical value for high-spin ferric ions, we find $\tau = 1.19 \times 10^{-10} \text{ sec}$. The uncertainty is about 3%.

We have estimated the spin correlation time at other temperatures and have found that within the

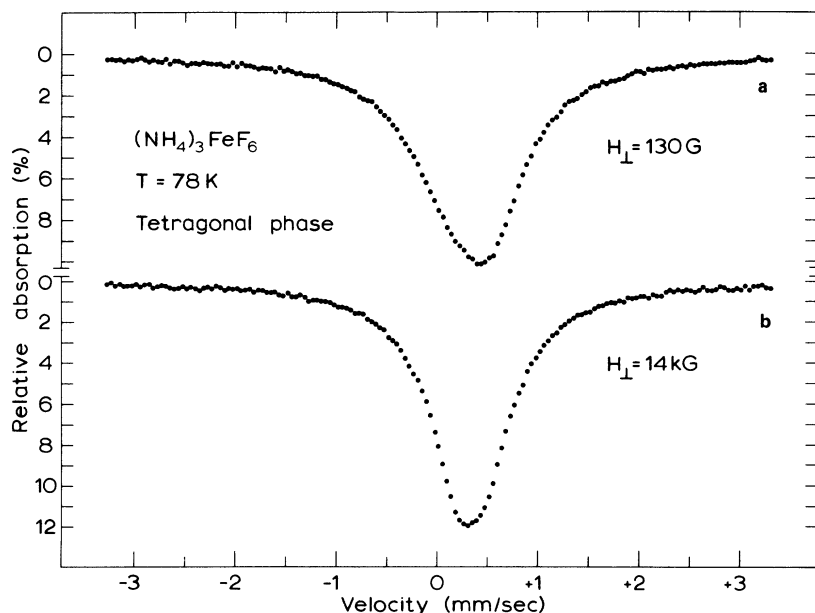


FIG. 3. Mössbauer spectra of $(\text{NH}_4)_3\text{FeF}_6$ obtained at 78 K. (a) $H_{\perp} = 130 \text{ G}$. (b) $H_{\perp} = 14.0 \text{ kG}$. (Note the asymmetry of the 130-G spectrum.)

uncertainty the spin correlation time is constant in the temperature interval 264–348 K. This means that spin-spin relaxation is fast compared to spin-lattice relaxation and thereby solely determines the spin correlation time.

The 130-G spectrum obtained at 78 K (Fig. 3) deviates distinctly from the best computer fit based on a diagonal hyperfine Hamiltonian. This fact supports our conclusion in Sec. IV B which says that $\mathcal{H}_{dd} + \mathcal{H}_{ex} > \mathcal{H}_{cub} + \mathcal{H}_{ax}$ in the tetragonal phase.

D. Magnetization Effects

It is evident that for $H_0 = H + \langle H_e \rangle_{av} \gtrsim 5$ kG, an additional broadening of the absorption lines should be found due to the Zeeman splitting of the nuclear levels. This effect was found at 273 K for $H > 8$ kG [Fig. 1(b)].

However, the effect is not observed at 78 K [Fig. 1(a)]. We have found the broadening also at 262 K, i. e., one degree below the transition temperature. Therefore the different broadenings at large fields are not connected with the phase transition. The difference is explained by the fact that the ionic magnetic moments and the hyperfine field H_e are antiparallel. As $\langle H_e \rangle_{av} = A \langle S_z \rangle_{av}$, we are able to calculate the temperature dependence of H_0 on the basis of the Curie law. We find

$$H_0(T) = \left[1 + A \frac{g\mu_B}{3kT} S(S+1) \right] H.$$

For Fe^{+3} in the high-spin state a typical value of A is -236 kG, causing a cancellation of the terms in the parentheses at $T = 92$ K. At 78 K, H_0/H

$= -0.18$, while at 273 K, $H_0/H = 0.66$.

V. CONCLUSION

We have shown that the shape of relaxation-broadened Mössbauer absorption lines depends strongly on certain terms of the ionic Hamiltonian. Particularly important are the relative magnitudes of the crystal-field interaction, the magnetic dipole-dipole interaction, and the ionic Zeeman interaction due to an applied field.

The change of the line shape, caused by application of external magnetic fields, can give information of the approximate magnitudes of the interactions between the ferric ion and its surroundings.

The present measurements on $(\text{NH}_4)_3\text{FeF}_6$ illustrates the importance of specific terms of the ionic and the hyperfine Hamiltonian for this special case. Other cases still remain to be investigated in detail.

At small applied fields the spectrum is Lorentzian. In accordance with our theoretical considerations, this suggests that the relaxation is isotropic. For large applied fields the spectra can be fitted with three Lorentzian lines, in agreement with the theory for longitudinal relaxation.

ACKNOWLEDGMENTS

The authors are grateful to K. O. Sørensen for evaluation of the computer program used for the fitting of the experimental results, and to Boye Olsen for drawing our attention to the field-dependent Mössbauer spectrum of $(\text{NH}_4)_3\text{FeF}_6$ and for placing the absorber material at our disposal.

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